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U.S. Army Toxic and Hazardous Materials Agency



DISPOSAL OF LIQUID PROPELLANTS (TASK ORDER NO. 0002; SUBTASK NO. 2)

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March 1990
Contract No. DAAA15-88-D-0001

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U.S. Army Toxic and Hazardous Materials Agency (USATHAMA)
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PREFACE

The U.S. Army is developing a liquid propellant that will possibly be used in certain applications as a replacement for conventional munitions. The propellant includes an oxidizer (hydroxylammonium nitrate), a fuel (triethanolammonium nitrate), and water. In anticipation of widespread (both continental U.S. and abroad) use of the propellant, USATHAMA began a research program to identify the procedures that could be implemented for disposing of the propellant in instances such as spills or destruction of excess or offspec liquid propellant. In this report the chemistry of the liquid propellant is reviewed and chemical, physical, and biological processes that result in the degradation of the propellant components and similar compounds are described. In addition, domestic and foreign regulations that pertain to environmental releases of the propellant and/or its degradation products are discussed. Those processes that may individually or in combination be useful for the safe disposal of the liquid propellants, liquid-propellant-contaminated soil, and sediments are discussed in this report. Recommendations for bench- and pilot-scale testing of the most promising technologies are also included.

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SUMMARY

A liquid propellant currently being developed by the U.S. Army consists of a mixture of an oxidizer, hydroxylammonium nitrate (HAN), a fuel, triethanolammonium nitrate (TEAN), and water. TEAN has been found to contain a hazardous impurity, N-nitrosodiethanolamine (NDELA), that is a carcinogen and poses an exposure hazard to personnel manufacturing TEAN. The purpose of this project is to provide the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) with a listing of potential methods that appear to be feasible for demilitarizing and disposing of the HAN-TEAN propellant residues on the basis of engineering, environmental, and cost considerations. In addition, methods for performing bench-scale evaluations and concepts for full-scale implementation of these potential methods are also discussed.

A comprehensive literature search was performed in which information was sought regarding the chemical/physical characteristics as well as degradation and disposal processes for the HAN-TEAN propellants and formation of NDELA. The major problem encountered at the outset of these investigations was the absence of published literature directly concerned with disposal or degradation of these propellant components, as interest in these compounds is relatively new. Therefore, methods for disposing of similar compounds such as triethanolamine, ammonium nitrate, and certain cutting fluids were also researched.

On the basis of the literature search results, three techniques including thermal destruction, biological treatment, and photolytic degradation have been identified as being potentially applicable for degrading the liquid propellant. Six criteria were formulated for use in guiding the process of selecting the degradation technology that is most appropriate for bench-scale evaluation. These criteria are technical feasibility, cost-effectiveness, potential for full-scale implementation, applicability in remote areas, potential for adverse environmental impact, and potential for compliance with environmental regulations.

On the basis of the above criteria, biological treatment appears to have the greatest potential for accomplishing degradation of HAN-based liquid propellant residues in an economical, environmentally safe manner in a wide variety of environments. Microbial degradation methods are currently being used for the disposal of various organic compounds (including explosives), and these processes are gaining wide acceptance. Available biological treatment systems that may be applicable for the degradation of liquid propellants include composting, aerobic bioreactor, rotating biological contactor, fluidized bed reactor, and trickling filter treatment.

Pertinent domestic environmental regulations were also reviewed and are summarized. Since the liquid propellant will also be used in the United Kingdom and West Germany, the environmental regulations of these two countries were also considered. This latter review was performed to ensure that demilitarization and disposal activities that may be performed in these countries comply with pertinent environmental statutes. The results of this regulatory review are included in this report.

Finally, recommendations have been included in this report regarding further evaluation (i.e., bench- and pilot-scale testing) of biological treatment.

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SECTION 1

INTRODUCTION

BACKGROUND

The United States Army is currently investigating the use of liquid propellants in large and medium caliber guns. By definition, a propellant contains all the necessary chemical components for combustion, as opposed to, for example, gasoline, which requires the addition of an oxidizer. The liquid propellant currently being investigated contains an oxidizer, hydroxylammonium nitrate (HAN), a fuel, triethanolammonium nitrate (TEAN), and water. Since both fuel and oxidizer are present in the propellant, the mixture is potentially dangerous. However, the liquid propellant formulation has been found, under normal handling conditions, to be quite stable and incapable of vigorous combustion except when ignited in a confined space such as the firing chamber of a gun.

Several liquid propellant formulations are being considered by the U.S. Army as replacements for conventional munitions. The most useful formulations to date are LGP 1845 and 1846, whose compositions are shown in Table 1 (1). These formulations contain stoichiometric quantities of fuel and oxidizer, and their complete combustion produces carbon dioxide, nitrogen, and water. The total energy of these propellants increases with decreasing water content. The thermal initiation temperatures of this formulation are reported to vary inversely with nitrate-ion concentration (2).

TABLE 1. PROPELLANT COMPOSITIONS

Propellant	Composition		
	HAN, wt. %	TEAN, wt. %	Water, wt. %
1845	63.23	19.96	16.81
1846	60.79	19.19	20.02

In a study (3) conducted by the U.S. Army Natick Research Center for the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), it was determined that the TEAN stock solutions prepared in early liquid propellant development studies were contaminated with N-nitrosodiethanolamine (NDELA). NDELA is a carcinogen (4, 5, 6) and could potentially pose an exposure hazard to workers manufacturing the TEAN and gun crews using the propellant. A contaminant study (7), however, concluded that proper manufacturing techniques nearly eliminate the production of NDELA. Nevertheless, the possible formation of NDELA during potential disposal scenarios and its subsequent environmental fate are not yet fully elucidated, and hence NDELA should be considered as a potentially hazardous impurity until waste treatment and handling methods are shown to negate this potential hazard.

In conjunction with anticipated widespread use of the HAN-TEAN liquid propellant, not only in the USA but abroad, the U.S. Army is undertaking efforts aimed at preventing environmental pollution at facilities involved in the handling or storage of liquid propellant. Under this pollution prevention program, procedures for demilitarization and disposal of the propellant will be developed, and the potential environmental impact of these procedures will be assessed.

In this report methods for demilitarizing and disposing of liquid propellant residues are described which, on the basis of engineering, environmental, and cost considerations, appear to be potentially applicable.

OBJECTIVES AND APPROACH

The study described in this report represents the first phase of establishing suitable procedures for preventing environmental pollution at locations where HAN-TEAN liquid propellants are employed.

The objectives of this study are stated below:

- ° Identify existing Department of Defense (DOD) data pertinent to demilitarization and disposal of the HAN-TEAN propellant.
- ° Review existing information regarding the chemical/physical characteristics, destruction, and disposal of the HAN-TEAN propellant and related compounds.
- ° Evaluate the technical feasibility, environmental considerations and cost-effectiveness of the potential demilitarization and disposal techniques.
- ° Evaluate the environmental impact of selected disposal techniques.
- ° Review domestic and foreign environmental regulations to ensure that the selected disposal activities comply with the pertinent environmental statutes.
- ° Make recommendations regarding further evaluation (i.e., bench- and pilot-scale testing) of selected disposal techniques.

In order to accomplish the objectives listed above, PEI Associates, Inc., initially collected information published by the Department of Defense which is pertinent to demilitarization and disposal of the HAN-TEAN propellant. Personnel in both the Ballistics Research Laboratory (BRL) and USATHAMA, who have conducted studies in this area, were contacted personally to discuss the information on the liquid propellant. Several publications provided by BRL were reviewed and the information has been incorporated into this report.

In addition, a comprehensive literature search was performed to find articles which address the chemical/physical characteristics, destruction, and disposal of the HAN-TEAN propellant, formation of N-nitrosodiethanolamine from triethanolamine, triethanolammonium nitrate, and/or diethanolamine. Chemical Abstracts, National Technical Information Service (NTIS), and Applied Science and Technology data bases were searched. Relevant papers were obtained, reviewed, and pertinent information has also been incorporated into this report. The major problem encountered during this information gathering process was the absence of literature concerned directly with disposal or degradation of these propellants, as interest in these compounds is relatively recent. Therefore, a search was made to find methods of disposing of similar compounds such as triethanolamine, ammonium nitrate, and cutting fluids and for methods used in the cosmetic industry. All pertinent references were added to the bibliography and pertinent data have been incorporated into this document.

The potential demilitarization and disposal techniques that were identified during the literature search were evaluated based on criteria such as technical feasibility, cost-effectiveness, potential for full-scale implementation, and environmental considerations. Those processes described in the literature which did not appear to be feasible were eliminated from consideration for future bench-scale evaluation.

Subsequent to the selection of potential demilitarization techniques, the possible environmental impacts of the selected techniques were estimated. Because of certain physical and chemical properties, the propellants could be potentially hazardous to the environment and these properties were taken into consideration during the assessment of the selected disposal techniques.

Pertinent domestic environmental regulations were reviewed. Since the liquid propellant will also be used in the United Kingdom and West Germany, the environmental regulations of these two countries were also considered. This review was to ensure that demilitarization and disposal activities which may be performed in these countries comply with the pertinent environmental statutes. The results of this regulatory review are included in this report.

Finally, recommendations have been included in this report regarding further evaluation (i.e., bench- and pilot-scale testing) of the selected techniques.

REPORT ORGANIZATION

Section 2 of this report addresses the physical and chemical characteristics of liquid propellant. This section also includes a discussion of the laboratory-scale and full-scale preparation of liquid propellant. Section 3 comprises a discussion of the formation of the impurity in the liquid propellant which is of greatest concern- a nitrosamine- and the associated health hazards of this impurity. Section 4 provides a comprehensive review of the literature on existing disposal and/or degradation technologies for liquid propellants and related compounds. Section 5 describes the potentially applicable disposal technologies for liquid propellants that were identified on the basis of the literature review. The guidelines formulated for use in selecting the disposal technologies which should be evaluated further are presented in Section 6. Section 6 also contains a summary of the potential environmental impacts of each of the three selected technologies. Section 7 summarizes the domestic and foreign regulations (for the United Kingdom and West Germany) which apparently pertain to the disposal of waste

liquid propellant and propellant-contaminated substances. Section 8 contains a brief discussion of the approach for bench-scale evaluations of processes which are potentially applicable for disposal/demilitarization of the liquid propellant and/or liquid propellant-contaminated soil and sediment.

SECTION 2

METHODS OF SYNTHESIS AND CHEMICAL AND PHYSICAL CHARACTERISTICS OF THE LIQUID PROPELLANT

The liquid propellant currently being developed consists of a mixture of hydroxylammonium nitrate (HAN), water, and the nitrate salt of an aliphatic amine (AAN) such as triethanolammonium nitrate (TEAN). Liquid propellants are still in the developmental stage and to date only relatively small batches have been prepared for use in research and development programs. Methods for full-scale production of propellant are currently being sought.

METHODS OF SYNTHESIS OF LIQUID PROPELLANT

Hydroxylammonium nitrate (HAN), prepared via the electrolysis of nitric acid, is commercially available as a high-purity, dilute, aqueous solution (8).

The AAN salt of triethanolammonium nitrate (TEAN) is prepared by adding triethanolamine dropwise to a vigorously stirred solution of 4 M HNO_3 (1). The acid is kept in an ice bath; the amine addition rate is controlled so that a temperature between 0° and 5°C is maintained throughout the course of the synthesis. The reaction is considered complete when a slight excess of amine is detected in the reaction vessel. The salt solution, which is colorless to pale yellow, is then heated to 50°C under vacuum to remove water and unreacted amine. The crystallized salt is recrystallized from distilled water and stored in a dessicator.

The propellant mixture is then prepared by combining aqueous solutions of HAN and TEAN. Since both dissolving the AAN salt and mixing of the AAN and HAN salt solutions are endothermic, no risk of thermal decomposition is encountered during propellant formulation and the mixtures are prepared without any special precautions (1). The fully formulated propellant is a clear, colorless, odorless liquid. In previous studies (9, 10), it has been shown that the initiation and ignition of HAN-AAN-water propellant mixtures is markedly influenced by common impurities such as chloride, iron, and copper ions. Hence, care should be taken to keep the propellant components and the containers free from impurities.

POSSIBLE TECHNIQUES FOR FULL-SCALE PRODUCTION OF LIQUID PROPELLANTS

Dilute solutions of HAN are currently manufactured in batch quantities in the United States by a proprietary process (11). These solutions have to be concentrated prior to mixing with the AAN to form propellants. Some of the production methods used to manufacture HAN include: 1) electrodialysis of hydroxylamine hydrochloride and nitric acid; 2) reaction of hydroxylamine sulfate and barium nitrate; 3) a three-step cation exchange process employing hydroxylamine sulfate and nitric acid; and 4) electrolytic reduction of nitric acid (11).

TEAN is not available commercially in large quantities at this time but can be produced in a simple acid-base neutralization of triethanolamine with nitric acid. The reaction is (11):



The results of the production studies of HAN and TEAN indicate that a full-scale production plant is technically and economically feasible and can be designed to manufacture liquid propellant.

PHYSICAL CHARACTERISTICS OF LIQUID PROPELLANTS

One of the most significant structural features present in HAN and TEAN is the hydroxyl group. The presence of this group in a molecule typically results in hydrogen bonding which decreases vapor pressure, increases boiling point, and enhances water miscibility (1).

HAN-water solutions at low HAN concentrations are described as aqueous solutions of a 1:1 electrolyte. As the HAN concentration increases, the system gradually changes from an aqueous solution to a molten salt that solidifies at temperatures well below the freezing point of either of its components (1).

TEAN-water solutions are more complex and do not exhibit homogeneity over the broad concentration range observed for HAN. TEAN behaves much like an ordinary ionic salt, forming saturated solutions that are approximately 5 molar at room temperature. The molecular weight and melting point of TEAN (212 and 80.4°C) are higher than those of HAN (96 and 48°C) (1).

The liquid propellants LGP 1845 and 1846 are homogeneous liquids and do not undergo any phase transitions over the entire temperature range of military interest. The propellant has a freezing point of -100°C and a thermal decomposition point (at ambient pressure) of 125°C. The HAN-TEAN formulation is odorless and the active ingredients, being salts, have no vapor pressure. The density of LGP 1845 is higher than that of LGP 1846 at all temperatures because the salt content of LGP 1845 is higher. The surface

tension of LGP 1845 is normally higher than that of 1846, and the values for either propellant are not substantially different from those of water.

At 25°C, the propellant exhibits the following physical properties:

Density: 1.430 g/cc
Kinematic viscosity: 4.965 cst
Dynamic viscosity: 7.100 cp
Surface tension: 66.901 dynes/cm
Glass transition: -100°C

Energetics at Loading Density of 0.2000 g/cc:

Flame temperature: 2469 K
Impetus: 898.3 J/g
Pressure: 207.80 MPa

CHEMICAL CHARACTERISTICS OF LIQUID PROPELLANTS

The liquid propellant can fume off if heated, but does not burn unless pressurized. To avoid initiation of fuming, the propellant and its components should not be stored at temperatures greater than 65°C for prolonged periods of time.

Either oxidizing or reducing agents will react with HAN-based propellants. When ignited at elevated pressure (in a confined space such as a gun barrel), the decomposition could progress to a very energetic reaction. Partial decomposition of liquid propellant (e.g., during fuming) produces toxic NO_x compounds.

HAN-based liquid propellant in its pure state looks like water, so any coloration indicates the presence of impurities and this would imply that the propellant should be handled with extreme caution. LGP 1845 and 1846 are electrically-conducting, ionic solutions, and therefore no static charge can be built up. To avoid chemical reactions, the propellant must not come into contact with acids or bases.

Liquid propellants react with most metals and many other common materials; therefore, great care must be taken in selecting containers in which to store the propellant. It should be stored in thin wall containers that will vent at 15 psi gauge (i.e., 15 psi above atmospheric pressure). This will prevent vigorous reaction initiation at high pressures.

After the injection of the liquid propellants into a high-pressure and high-temperature environment (gun barrel), the propellant decomposes to yield gaseous combustion products. The properties of the principal products arising from combustion of LGP 1845 and LGP 1846 were computed by Kounalakis and Faeth (12) and are summarized in Table 2-1 for pressures of 1 MPa, 10 MPa, and 100 MPa. Both LGP 1845 and 1846 yield identical combustion products which include nearly 70% water vapor.

TABLE 2-1. COMBUSTION PROPERTIES OF HAN-BASE MONOPROPELLANTS (12)^a

Propellant	LGP 1845 ^b			LGP 1846 ^c		
Pressure (MPa)	1	10	100	1	10	100
Reactant density (kg/m ³)	1452	1454	1476	1430	1432	1454
Combustion product properties						
Density (kg/m ³)	1.30	12.9	129	1.36	13.5	135
Temperature (K)	2133	2152	2163	2027	2039	2045
Composition (% by volume) ^d						
Water vapor	68.8	69.2	69.3	70.6	70.8	70.9
Carbon dioxide	12.7	12.9	13.0	12.2	12.3	12.3
Nitrogen	17.3	17.4	17.4	16.5	16.5	16.6

^a Adiabatic, constant pressure combustion, with the liquid reactant at 298.15 K.

^b Reaction composition (% by mass): HAN, 63.2; TEAN, 20; and H₂O, 16.8.

^c Reaction composition (% by mass): HAN, 60.8; TEAN, 19.2; and H₂O, 20.0.

^d Major species only. Minor species include: CO, H₂, NO, OH, and O₂.

SECTION 3

CHEMISTRY AND TOXICOLOGY OF N-NITROSODIETHANOLAMINE

One of the major constituents of LGP 1845 and 1846 is the nitrate salt of triethanolamine (TEA) or triethanolammonium nitrate (TEAN). As mentioned in the previous section, the synthesis of TEAN involves the acid-base neutralization of triethanolamine and nitric acid. It is believed that during the course of this reaction, however, a hazardous impurity, N-nitrosodiethanolamine (NDELA) or N-nitrosamine can be formed. N-nitrosamines are organic compounds which have been found to be acutely toxic, carcinogenic, mutagenic, or teratogenic when tested in a variety of animals (13, 14, 15).

MECHANISM OF NITROSAMINE FORMATION

Nitrosamines are typically formed by the reaction of nitrite (NO_2^-) or a nitrosating reagent with secondary or tertiary amines under acidic conditions. The conversion of TEA to NDELA in aqueous nitric acid is presumed to be a two-step process. The first step is the dealkylation of the tertiary amine (TEA) to the secondary amine, diethanolamine (DEA). The second step is the reaction of DEA with a nitrosating agent(s) present either in nitric acid or TEA to yield NDELA (7).

It has been shown that secondary amines undergo nitrosation approximately 10,000 times faster than tertiary amines in the presence of nitrous acid at pH 3.4 and 25°C (16). The mechanism of secondary amine nitrosation is shown in Figure 3-1 (17).

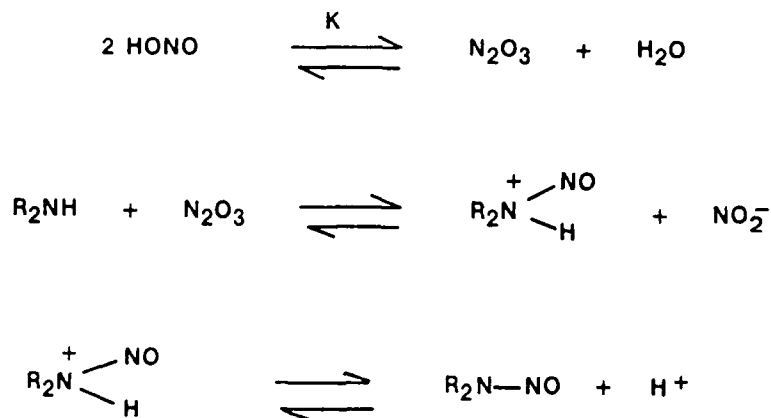


Figure 3-1. Mechanism of secondary amine nitrosation (17).

A study was performed by Battelle Columbus Laboratories (7) in which four aspects of the acid-base neutralization reaction for forming TEAN were examined to determine what parameters must be controlled in order to minimize production of NDELA. The process variables studied were order of addition, temperature, purity of the amine, and concentration of amine. The results of this study showed that formation of NDELA was kept at a minimum when the neat amine was used at 97% purity, when the temperature was kept below 5°C (preferably 0°C), and when amine was added to the acid. It was found that order of addition was the most significant variable (7). It has been stated (18) that NDELA is completely degraded by the HAN component of LGP 1845 or LGP 1846.

The findings cited above indicate that the amount of NDELA formed during synthesis of TEAN can be markedly reduced and that NDELA is degraded by the HAN component of the fully formulated propellant. However, data are not available which rule out potential NDELA formation during the shelf-life of liquid propellant or during potential disposal scenarios. The environmental fate of liquid propellant is not yet fully elucidated and the possibility for NDELA formation as the propellant reacts with components of the environment must be considered.

Numerous studies have documented nitrosamine formation in nature under a variety of environmental conditions. The two major environmental reactants in the formation of nitrosamine are secondary amines and nitrite. Secondary amines are found throughout the animal and plant kingdoms and are also formed during the decomposition of natural and synthetic organic residues. Nitrite may arise in the environment during the microbial transformations of ammonia or nitrate or through manufacturing processes (19). Since both of the above reactants are present in the liquid propellant, there is always a possibility that these components can enhance the formation of nitrosamine when the propellant is exposed to the environment.

Literature articles on formation of nitrosamine under various environmental conditions were reviewed prior to preparing this report. Nitrosamine contamination has been found in a number of commercial products including detergents, cosmetics, shampoos, cutting fluids, and hydraulic fluids. A summary of processes which give rise to nitrosamines is given in the following paragraph.

The formation of nitrosamines under experimental conditions has been demonstrated in amended municipal sewage and lake water (20, 21), feedlot manure (22), and agricultural chemicals (23, 24). Furthermore, several studies have suggested that nitrosamines are persistent in natural ecosystems (25) and can be readily leached from soil (26, 27). NDELA has recently been found in a variety of products such as cutting fluids (28, 29), grinding fluids (30, 31), shampoos, cosmetics, and lotions (32, 33) which contain diethanolamine.

Recent evidence suggests that microorganisms are involved in one or more stages of nitrosamine formation in nature. It has been reported that several

bacterial species form nitrosamines in vitro (34-36). Microbially-mediated reactions in aqueous and soil systems occur over a broad range of pH from approximately 4.0 to 8.0. Green et. al. (37) demonstrated N-nitrosodimethylamine (NDMA) formation at pH 4.7 and 5.6 in soils amended with sewage, dimethylamine, and nitrite. It has been reported that the reaction rate for formation of NDMA increases 10-fold for each unit drop in pH down to pH 3.36 (38). A considerable volume of literature has been published on N-nitroso compounds in recent years which includes chemistry, reaction mechanisms, and biological and chemical aspects of nitrosamines (39-49).

HEALTH HAZARDS OF NITROSAMINES

Although N-nitrosamines have been known since the nineteenth century, it was not until quite recently that they became the subject of intensive toxicological investigations. The upsurge of interest has resulted from the discovery (50) that nitrosamines are powerful carcinogens and cause cancer in rats. There has been a growing interest in the occurrence and in vivo formation of N-nitrosamines, especially in connection with cancer in man. Much information has been published in this area, mostly concerning animal bioassay experiments (4-6, 51-54).

Nitrosamines act systemically and produce cancer in a wide variety of organs of many species (55). Experimental work in the rat indicates that most organs are sensitive to the carcinogenic action of one or more nitroso compounds and recent reports suggest that this may be true for other species. Several reports indicate that nitrosamines may be present in the human environment in a variety of situations (56). Potential human exposure to

nitrosamines is possible by ingestion (various food products), skin absorption (cosmetics), and (to a lesser extent) inhalation. As of June 1980, the FDA had analyzed 335 cosmetic products for NDELA and found that 42 percent were contaminated with this carcinogen (57). Hence man may absorb small amounts of nitrosamines which are present in the environment as a result of natural or anthropogenic activities. There is to date no published report of any animal species that is resistant to carcinogenesis by these agents and hence there is no reason to believe that man is not susceptible.

SECTION 4

SUMMARY OF CHEMICAL, BIOLOGICAL, AND PHYSICAL REACTIONS WHICH LEAD TO DEGRADATION OF LIQUID PROPELLANTS AND RELATED COMPOUNDS

Liquid propellants are under evaluation for Army applications as a substitute for nitrocellulose in ball powder mixtures. Follow-up programs will most likely require substantial increases in the quantities of these propellants now being produced. With this anticipated increase in production and usage, the potential for spills and contamination of the environment by liquid propellants can be expected to increase proportionally. Therefore, development of disposal techniques which can be implemented in the possible situations giving rise to waste liquid propellant is warranted. Some of the potential scenarios which may involve the disposal of liquid propellants are:

- ° Disposal of propellant at the end of its life. At present, BRL is estimating the shelf life of the propellant to be approximately 20 years.
- ° Disposal of contaminated propellant (1 gallon to several thousand gallons could become contaminated).
- ° Disposal of water used to extinguish a fire involving stored liquid propellant.
- ° Disposal of contaminated soil resulting from propellant spills during use or transportation.
- ° Disposal of spent propellant containers.

A comprehensive literature review was conducted to identify existing information regarding disposal techniques for liquid propellants. As expected, it was determined that the literature concerned directly with dis-

posal of liquid propellants was not available. To date, very little work has been accomplished with respect to disposal or degradation of HAN-based propellants because the interest in these compounds is relatively recent. However, a considerable amount of work has been performed to develop methods for disposing of similar compounds such as triethanolamine, ammonium nitrate, and mixtures containing similar amines (for example, cutting fluids and cosmetics). Therefore, in addition to searching for liquid propellant disposal methods, the literature search also concentrated on the disposal techniques that are currently used for disposing of related compounds such as those cited above. In the paragraphs which follow, potentially applicable disposal technologies that are reported in the literature are described.

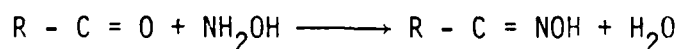
DEGRADATION OF AMMONIUM NITRATE PROPELLANTS

Kaplan, et. al. (58) studied the biodegradability of four ammonium nitrate propellants: trimethylammonium nitrate (TMAN), isopropylammonium nitrate (IPAN), triethanolammonium nitrate (TEAN), and hydroxyl- ammonium nitrate (HAN). Results of the Ames test indicated that none of the four ammonium nitrate propellants was mutagenic. These findings suggest that development of a biological approach to treat process waters containing these compounds would be feasible. The results of the study by Kaplan et al. indicate that TMAN, TEAN, and IPAN are readily biodegraded. Under both aerobic and anaerobic conditions, these three amines were decomposed without any significant formation of intermediates. TEAN was decomposed under aerobic conditions in batch and continuous cultures in a variety of media, and under anaerobic conditions in batch systems and in continuous flow systems under denitrification conditions. The mixture of microorganisms used for the

active systems (batch, continuous, and soil) was obtained from aerobic and anaerobic sewage sludge and soil.

Kaplan (58) found that HAN is chemically unstable above a pH of about 5.9. With a demonstrated instability above pH 5.9 and with numerous potential reactions in soils, it is expected that HAN would not persist under most environmental conditions.

Other reports in the literature indicate that hydroxylamine rapidly disappears from soils through a number of chemical reactions with inorganic and organic soil components (59, 60). The HAN was converted to either inorganic forms of nitrogen (i.e., NH_4^+ , NO_2^- , NO_3^-), or it was fixed by the organic matter in the soil with a subsequent release of gaseous forms of nitrogen. It was postulated that the fixation of the hydroxylamine occurred through the formation of oximes when carbonyl groups in the soil organic matter react with NH_2OH (59):



Crystalline hydroxylamine suffers rapid deterioration at room temperature to yield ammonia, water, nitrogen, and nitrous oxide as principal products (61). Aqueous solutions of hydroxylamine deteriorate when coming in contact with atmospheric oxygen (61). This phenomenon of autooxidation should enhance the degradation of HAN under aerobic conditions during biological treatment.

Van Dijk and Priest (62) observed a significant and irreversible change in the HAN spectrum at pressures near 6 Kbar and temperatures near 90°C. This change was interpreted to be the result of thermal decomposition occurring within the sample.

Balandin, et. al (63) reported that cells of Monoraphidium braunii metabolized hydroxylamine, reducing it stoichiometrically to ammonium ion in darkness. In light, however, the rate of hydroxylamine disappearance was slightly higher than that of the ammonium release to the medium, indicating photooxidation of hydroxylamine.

DEGRADATION OF N-NITROSO COMPOUNDS

Numerous reports exist in the literature regarding the in vivo and in vitro formation of nitrosamines from the reaction of nitrite with susceptible amines (see Section 3). N-nitrosamines are stable compounds and are difficult to destroy once they are formed. They are stable in neutral and strong alkaline solutions in the absence of light (64). When exposed to ultraviolet light, however, nitrosamines decompose and form aldehydes, nitrogen, and nitrous oxide; or alternatively, an amine and nitrous acid may be formed depending on the wavelength used. The apparatus and conditions for the photochemical destruction of nitrosamines in solution in the presence of an HNO_2 scavenger have been described in the literature (65,66).

A pilot-scale solar UV radiation photoreactor system has been used at the Army sites to treat nitrosodimethylamine (NDMA)-contaminated well water (67). NDMA concentrations were reduced from 80 ppb to less than 1 ppb with treatment times varying from 4 hours in summer to 72 hours in winter. Another study dealing with photochemical nitrosamine degradation (66) used two different types of apparatus. One apparatus utilized ultraviolet irradiation through pyrex glass (using wavelengths > 280 nm), giving low-intensity irradiation. The other apparatus used quartz instead of glass, which permitted wavelengths < 280 nm to be transmitted. The glass apparatus was shown to

degrade about 0.1 mol of nitrosamines in 24 hours, while the quartz apparatus showed degradation capacities of 0.15 mol per 24-hour period.

Studies of inhibition of nitrosamine formation have involved the use of substances which compete with the amine for nitrosating species. In addition, several authors have reported on the ability of ascorbic acid (Vitamin C) to inhibit nitrosamine formation (16). Mirvish et al. (68) have suggested that the potential danger of ingesting drugs or certain food substances that can be nitrosated may be reduced by the addition of ascorbic acid.

Inhibition of nitrosamine formation by phenols (e.g., alpha-tocopherol) occurs by reduction of nitrate to nitric oxide, which is nonreactive, or by removal of nitrite via C-nitrosation (16). Alpha-tocopherol (vitamin E) has been shown to react with nitrites (acting as a nitrite scavenger) to prevent nitrosamine formation (69). Sulfur compounds, vitamin A, urea, caffeine, and ethanol have also been shown to be in vitro inhibitors of nitrosamine formation (16).

N-nitrosamides decompose in aqueous acid by both denitrosation and deamination pathways (70). At alkaline pH, nitrosamides decompose to diazoalkanes (38). The rate of decomposition increases with increasing pH and varies with amide structure.

DEGRADATION OF OTHER RELATED COMPOUNDS

In conjunction with the widening use of secondary and tertiary amines, which can react with nitrites to form nitrosamines, degradation characteristics of these compounds have been assessed in several studies.

Microbial degradation of diethanolamine (DEA) and triethanolamine (TEA) has been investigated using sewage microorganisms (71). Pure culture growth and biochemical oxygen demand studies showed that both TEA and DEA were degradable. Additional studies concerning the biodegradation of TEA and DEA have also been conducted using a yellow gram-negative rod (72). Figure 4-1 illustrates the proposed metabolism pathway for TEA and DEA.

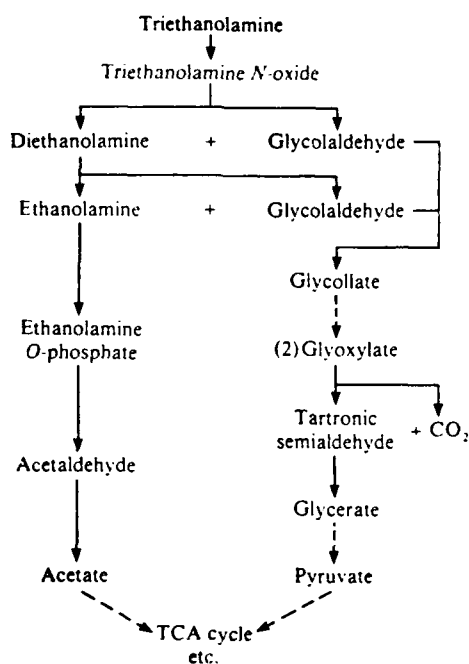


Figure 4-1. Proposed pathway for metabolism of TEA and DEA by the yellow gram-negative rod (72).

The methods for the reduction and/or destruction of nitrosamines in cutting fluids (73) and cosmetics production (74, 75) have also been investigated for commercial applications. Results of cutting fluids (73) investigations suggested several ways to reduce nitrosamine formation such as:

- ° Avoid acid-splitting as a disposal procedure.

- ° Remove nitrite from the fluid and/or scavenging adventitious nitrosating agents.
- ° Avoid unnecessary heating.
- ° Add preservatives (e.g., formaldehydes) to the diluted fluid instead of the commercial concentrate (formaldehyde strongly catalyzes the formation of nitrosamines from nitrite and secondary amines).
- ° Minimize concentrations of catalytically active metal complexes.
- ° Replace nitrosatable amine additives with substitutes that are resistant to nitrosamine formation.

In a patented process (76), ammonium-nitrite-containing waste water was treated by means of wet thermal decomposition in the presence of a catalyst. The process demonstrated that the NH_4^+ and NO_3^- ions can be efficiently decomposed when subjected to wet thermal decomposition.

USATHAMA has also investigated the potential for composting of explosives and propellant-contaminated sediments (77-81). Field-scale demonstration of static pile composting to decontaminate nitrocellulose (NC)-contaminated soils was conducted at Badger Army Ammunition Plant (BAAP) (81). Another field-scale demonstration of composting was conducted at Louisiana Army Ammunition Plant (LAAP) (80) to decontaminate soils containing 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)-contaminated lagoon sediments.

The treatment process involved mixing contaminated soils or sediments with straw/horse manure, alfalfa, horse feed, and wood chips to enhance microbial degradation. After 153 days, total explosives at the LAAP facility were reduced by 99% (from 17,872 to 74 ppm) in the thermophilic (55°C) pile. At the BAAP facility, NC concentrations were reduced from 13,086 ppm to 16 ppm after 101 days in a thermophilic pile.

The results of these field demonstrations indicate that composting is a feasible technology and should be evaluated for remediating propellant- and explosives-contaminated soil and sediment.

SECTION 5
TECHNOLOGIES POTENTIALLY APPLICABLE TO THE DISPOSAL
OF LIQUID PROPELLANT

On the basis of the literature review and discussions with BRL and USATHAMA personnel, three potential technologies have been identified as being potentially useful for the disposal or degradation of HAN-based liquid propellants. The three technologies are thermal destruction, biological treatment, and photolytic degradation. In this section each of these technologies is described, the status of the technologies is summarized, the current applications are reviewed, and certain pros and cons associated with the use of each technology are presented. At the conclusion of this chapter, each of these technologies are rated based on technical feasibility, cost-effectiveness, potential for full-scale implementation, and environmental considerations. On the basis of this comparison of technologies, potential demilitarization and disposal technologies have been selected and recommended for further study.

I. THERMAL DESTRUCTION

Thermal treatment (or incineration) involves the use of high temperature thermal oxidation as the primary means of destroying or detoxifying hazardous wastes. Thermal treatment offers the potential for essentially complete destruction of the original organic waste. The destruction and removal efficiency achieved for waste streams incinerated in properly operated thermal processes often exceeds the 99.99 percent regulatory requirement for hazardous wastes.

Morton-Thiokol, Inc., has prepared HAN-based liquid propellants for several years and has been incinerating the liquid propellant wastes. Although the products of combustion of the pure propellant have been well characterized, the combustion products of solid and liquid mixtures containing liquid propellants have not been thoroughly characterized. It should be noted that with any thermal treatment process, consideration must be given to the fact that incomplete combustion of the liquid propellant can result in the formation of NO_x , HNO_3 , and possibly nitrosamines.

Some of the advantages of thermal treatment are:

- ° The volume and weight of combustible waste are reduced to a fraction of its original size.
- ° Waste can be incinerated on site, without having to be transported to a distant area.
- ° Products of complete combustion are not a threat to human health.
- ° Available air pollution technologies can control potential particulate emissions.
- ° Energy released during combustion can conceivably be recovered.

However, incineration does not solve all the waste disposal problems.

The disadvantages of incineration include:

- ° High capital costs.
- ° Combustion temperatures must be maintained carefully to ensure complete destruction.
- ° Some materials may require supplemental fuel to attain mandated efficiencies of destruction.
- ° Some metals may volatilize during incineration (e.g., As, Hg, Pb, Sn), and these emissions might be difficult to remove using conventional air pollution control equipment.
- ° Halogen compounds such as HCl , HBr , or HF may attack refractory material and/or impact air emissions when thermally treated.
- ° Aqueous wastes may not be suitable for certain thermal destruction methods.

Although several methods are available for the thermal oxidation of hazardous materials, three thermal destruction methods have been identified which may have the most potential for the disposal of liquid propellants. These thermal treatment methods are: rotary kiln incineration, liquid injection incineration, and fluidized bed incineration. Each of these thermal oxidation processes are discussed below.

ROTARY KILN INCINERATION

Technology Description

Rotary kiln incinerators are inclined cylinders used in the combustion of organic solids and sludges (82). Rotary kiln incinerators are typically fueled by natural gas, oil, or pulverized coal, and are usually used in conjunction with an afterburner and a wet scrubber emission control system (83). Wastes are injected at the top of the kiln and pass through the combustion zone as the kiln rotates (to create turbulence and improve combustion). Retention time within the combustion chamber varies from a few minutes to more than an hour. Exhaust gases from the kiln are typically ducted to a secondary combustion chamber (afterburner) for further oxidation. Residues which are generated in this process include ash from the low end of the kiln, stack gases, and brine solution from the wet scrubber (82).

Applicability/Limitation

Most types of solid, liquid, and gaseous organic wastes or mixtures of these types of wastes can be treated with this technology. However, rotary kiln systems are not well-suited for treating wastes with high inorganic salt content. These systems are susceptible to thermal shock, have a relatively low thermal efficiency, can generate high particulate emissions which must be controlled, and are costly to install.

Technology Status

Rotary kiln incinerators, both fixed and mobile, are commercially available and are in wide use. They have been shown to be highly effective for destroying wastes containing PCBs, dioxins, obsolete munitions, and other toxic substances. As indicated elsewhere in this report, a transportable rotary kiln system is currently being used to treat munitions-contaminated soils at the Louisiana Army Ammunition Plant (LAAP). The performance of this system at LAAP is briefly summarized below:

- ° A total of 32,000 tons of soil/clay was incinerated through July 9, 1989.
- ° Maximum daily throughput of 426 tons on June 17, 1989.
- ° Maximum weekly throughput of 2,785 tons for June 24-30, 1989.
- ° Average operating factor of 85% since April 28, 1989.
- ° Best weekly operating factor of 98.8% (June 24-30, 1989).

LIQUID INJECTION INCINERATION

Technology Description

Liquid injection incineration entails introduction of liquid waste material into the combustion chamber by means of specially designed nozzles (84). For efficient combustion, the liquid is typically atomized prior to entering the combustion chamber. Following combustion, the resulting gases are cooled and treated to remove particulates and to neutralize acid gases. Pretreatment, such as blending, may be required to allow some wastes to be introduced through special nozzles to provide efficient mixing with the oxygen source and to maintain a continuous, homogeneous waste flow. Combustion zone residence time typically ranges from 0.5 to 2.0 seconds with operating temperatures ranging from 1200° to 3180°F (85).

Applicability/Limitation

Liquid injection incineration can be applied to pumpable organic wastes including wastes with high moisture content. Particle size is very critical for successful operation. The use of liquid injection incinerators is limited to wastes which can be atomized and is generally not suitable for wastes with high inorganic (metals, salts) content.

Technology Status

This process is in widespread use and has been used to destroy a wide variety of chemicals, including PCBs, solvents, still reactor bottoms, polymer wastes, and pesticides.

FLUIDIZED BED INCINERATION

Technology Description

The fluidized bed incinerator consists of a cylindrical vessel containing a bed of inert, granular, sand-like material. Solids, sludges, and liquids can be injected directly into the bed or at its surface. Air is blown through the granular bed materials until they are "suspended" and able to move and mix in a manner similar to a fluid (86). Combustion occurs within the fluidized material. The particulate matter exiting the combustion zone is usually separated in a cyclone and exhaust gases pass through an afterburner to destroy vapor-phase residuals. Residence times in the fluidized bed are generally on the order of 12 to 14 seconds for a liquid waste, with operating temperatures ranging from 900° to 1700°F (83).

Applicability/Limitation

Advantages of this technology include excellent heat transfer to the materials being incinerated and a long residence time. This treatment is

ideal for slurries and sludges but not for bulky or viscous wastes. Some refractory wastes may not be fully destroyed since these units operate at comparatively low combustion temperatures. Operating costs are relatively high.

Technology Status

The fluidized bed technology is used in the United States by the paper industry and in Europe in many locations. The technology has also been used to treat municipal wastewater treatment plant sludge, oil refinery waste, pharmaceutical waste, phenolic waste, and methyl methacrylate.

II. BIOLOGICAL TREATMENT

Biological treatment, or biodegradation, involves the bio-oxidation of organic material using microorganisms. Biological treatment of contaminated soil or sediment usually relies on microbes indigenous to the contaminated soil; however, these indigenous colonies are sometimes enriched with other microbial cultures to accomplish successful treatment. The desired level of microbial activity is often obtained simply by addition of appropriate nutrients and by increasing oxygen transfer within the contaminated environment.

Biological treatment is dependent upon a number of environmental factors such as nutrient levels, pH, temperature, dissolved oxygen, and toxicity of waste to be treated. Wastes in any form--solid, aqueous, and gaseous--can be treated biologically. Contaminated sludges and soils can be biologically treated in situ or excavated and treated by solid-phase and slurry-phase bioremediation processes. Enhanced in situ biodegradation is being used for sites where soil and/or ground water are contaminated with readily biodegradable organics such as gasoline and diesel fuel (82, 87). As discussed

in Section 4, studies to develop microbial degradation processes for the ammonium nitrate propellants in aqueous and soil systems under a variety of conditions have already been performed. Also as indicated in Chapter 4, it has been shown that both TEAN and HAN are biodegradable.

The advantages of biological treatment are:

- ° The technology is cost-effective (in some cases, cost is as little as 10 to 20% of incineration).
- ° Biodegradation can readily be implemented at almost any location.
- ° It can degrade recalcitrant compounds.
- ° Compounds resulting from microbial degradation are typically innocuous.

The disadvantages of biological treatment are:

- ° The rate of biodegradation is often slow.
- ° Nutrient levels, pH, and other operating conditions must be controlled carefully.
- ° Depending upon how carefully conditions are optimized and then controlled, some compounds may be only partially degraded.
- ° Microbial populations are sensitive to high concentrations of certain chemicals (e.g., metals, inorganics, and organics).

Through searching the literature, several different biological treatment processes have been identified which appear to have potential applicability to the disposal of liquid propellants. The technologies are: 1) composting, 2) aerobic bioreactor process, 3) trickling filter, 4) rotating biological contactor, and 5) fluidized bed reactor. Each of these processes are discussed below.

COMPOSTING

Technology Description

Composting is a biological process used typically for the treatment of wastes with high concentrations of biodegradable organic solids (88). The

contaminated wastes are blended with a bulking agent (wood chips, saw dust, etc.) to provide void space for aeration and to support the compost matrix. Waste destruction and conversion are achieved by the use of thermophilic aerobic microorganisms which occur naturally in decaying organic matter. The optimum temperature range for composting is 35° to 60°C.

Composting processes typically entail four steps (86):

1. Mix wastes with a bulking agent to enhance aerobic conditions.
2. Introduce air and indirect heat to promote thermophilic conditions.
3. Allow waste to stabilize.
4. Separate the bulking agent from the stabilized waste.

There are three basic types of composting (82): open windrow systems, static windrow systems, and in-vessel (reactor) systems. The open windrow system consists of stacking the compost into elongated piles. Aeration is accomplished by tearing down and rebuilding the piles. The static windrow system also involves long piles of compost; however, the piles are aerated by a forced-air system. Finally, the in-vessel system involves placing the compost into an enclosed reactor. Aeration can be accomplished by tumbling, stirring, or forced aeration.

Applicability/Limitation

Many organic chemicals can be treated by composting. The fate of inorganics (cyanides, sulfides, and metals), however, is not yet certain. Compounds that have limited aqueous solubility are not readily metabolized by microorganisms. Wastes must not have excessive moisture because too much moisture will slow processing by absorbing the heat needed for biological growth. Climatological factors are also important since they affect metabolic rates, odor emission, and drying rates.

Technology Status

Composting has been used in the municipal sector for the conditioning of sewage sludge. It has also been used to treat a variety of industrial solid wastes and has been demonstrated at field-scale by USATHAMA (as mentioned in Section 4) for composting explosives- and propellant-contaminated sediments.

AEROBIC BIOREACTOR

Technology Description

This method involves confining and decontaminating soil in a biological reactor. The reactor consists of a container having the bottom, sides, or walls continuously connected together and a cover suitable for excluding liquids and solids from entering the container. The impermeable sides and bottom prevent contaminants from leaking out of the container. At least two treatment courses, each comprising a layer of the contaminated solids, are distributed in the container and subtended by the gas distributing system. The thickness of the solid layer is adjusted to permit a sufficient quantity of oxygen gas to maintain the layer aerobic. The moisture content of the soil is adjusted from 2% to about 90% (optimum is from 40 to 60%) of field saturation, and the nutrient content is adjusted to provide sufficient phosphorus and nitrogen nutrients to ensure that the microorganisms in the soil are not nutrient-limited.

The oxygen in the gas diffuses into the layer of the contaminated soil or other solid where it is utilized by a microorganism to metabolize the organics. Volatile metabolism products, such as carbon dioxide, in the layer of contaminated particulate matter diffuse into the gas containing oxygen and are exhausted from the gas distributing system.

Applicability/Limitation

The process is suitable for biodegrading organic contaminants, particularly petroleum products or hydrocarbons on soil. The design of the system is fairly simple. It can easily be adopted on site by excavating a pit in the earth and lining the pit with a flexible lining impervious to the organic compound and to water. This technology is suitable for treating contaminated solids.

Technology Status

The technology has been used at several service stations to degrade hydrocarbon-contaminated soil.

TRICKLING FILTER

Technology Description

This technology can be used for treating large quantities of aqueous wastes. The liquid wastes are sprayed over a bed of rocks or a synthetic medium upon which a slime of organisms is grown (89). The organic material present in the liquid waste is degraded by a population of microorganisms attached to the filter medium. Organic material from the liquid is adsorbed onto the biological film or slime layer. In the outer portions of the biological slime layer, the organic material is degraded by aerobic microorganisms. As the microorganisms are grown, the thickness of the slime layer increases, and the diffused oxygen is consumed before it can penetrate the full depth of the slime layer. Thus, an anaerobic environment is established in the deeper layers of the biomass.

Applicability/Limitation

This technology is suitable for treating aqueous wastes which contain organic contaminants. Trickling filters are efficient in removing alcohols,

phenols, phthalates, cyanides and ammonia. Trickling filters have very large treatment capacities and can therefore handle large volumes of aqueous waste. The disadvantage of trickling filters is the requirement for a very uniform flow rate and a consistent temperature above 0°C. Odors from the filter and flies can be a problem. If the filter must be covered for odor control, forced air ventilation is often necessary.

Technology Status

The technology has been typically employed to treat municipal and industrial liquid wastes. It has also been utilized to biodegrade leachate from hazardous waste lagoons. A version of the trickling filter was recently demonstrated under the U.S. Environmental Protection Agency's Superfund Innovative Technology Evaluation (SITE) program (90).

ROTATING BIOLOGICAL CONTACTORS

Technology Description

Rotating biological contactors (RBCs) aerobically treat aqueous waste streams, especially those containing alcohols, phenols, phthalates, cyanides, and ammonia. The process consists of primary treatment for solids removal followed by the rotating biological contactor where the waste stream comes into contact with the microbial film and the atmosphere. The rate of rotation can be varied to optimize oxygenation of the biomass and the contact time between the biomass and the wastes to be degraded. Following RBC treatment the effluent is typically sent to a secondary clarifier.

Applicability/Limitation

Rotating biological contactors have been used for some time. Depending upon the type of waste, the results obtained using the RBC vary. Highly

chlorinated organics, aliphatics, amines, and aromatic compounds are particularly difficult to degrade using this technology. Recently, however, RBCs coated with white rot fungus (Phanaerochaete chrysosporium) have shown promise for degrading recalcitrant compounds. Some heavy metals and organic chemicals are harmful to the organisms.

Technology Status

Conventional RBC technology has been used for some time. Other types of RBC technology (e.g., white rot fungus) are under development.

FLUIDIZED BED REACTOR

Technology Description

The fluidized bed reactor relies on immobilization of microbes on a hydraulically expanded or "fluidized" bed of inert (silica sand) or active (activated carbon) media particles. In this process, the contaminated wastewater and recycled effluent pass upward through the media bed at a velocity sufficient to expand the bed beyond the point at which the frictional drag is equal to the net downward force exerted by gravity. Once at or beyond this point of minimum fluidization, the media particles are individually and hydraulically supported and provide a working interface for the passage and biodegradation of organic contaminated liquids. The fluidized bed reactor provides excellent retention and biomass interface time, and this dynamic system reduces the chances of bacterial growth inhibition due to buildup of toxic by-products or inhibitory feed inputs. Apparently this system accumulates a large biomass concentration in the fluidized bed, which allows for the efficient degradation of complex organic compounds at a shorter liquid contact time or hydraulic retention time (HRT) relative to more conventional biological systems.

Applicability/Limitation

The technology is used in fermentation processes and for treating aqueous wastes contaminated with organics. The limitation of this technology is that it can be used only for liquid wastes.

Technology Status

The technology is conventional.

III. PHOTOLYTIC DEGRADATION

Technology Description

Ultraviolet (UV) photolysis is a process in which electromagnetic energy is employed to disrupt covalent bonds, thereby altering the molecular structure. Absorption in the UV range causes the molecule to be elevated to a higher energy state, which can result in the breaking of chemical bonds and the rearrangement or dislocation of molecular structures.

Photochemical degradation is a zero-order reaction in which photoexcitation is the rate-determining step. The UV emissions of any one lamp are constant, and under appropriate conditions the emitted light energy in the absorbing region (typically up to 360 nm) can be utilized totally. When the concentration of the substrate is high enough to ensure 100% utilization of the light flux, the operation of an apparatus is most efficient, and the decrease in substrate concentration is linearly proportional to the time of irradiation. When the substrate concentration falls below that of 100% absorption, the photolysis rate gradually slows down, exhibiting a pseudo-first-order curve (65).

Thus, the efficiency of a photolysis apparatus is dependent on: 1) the type and age of the lamp, 2) the quality of the light transmitter, 3) the concentration of the solution and the length of the light path, 4) the

arrangement of the light source, and 5) the quantum efficiency of substrate decomposition.

Applicability/Limitation

Several UV-based processes have been described in the literature including (84):

- UV photolysis preceded by solvent extraction
- UV photolysis in combination with ozonation
- UV photolysis preceded by thermal desorption

The advantages of photolytic degradation are:

- It is a fairly simple and efficient method.
- Raw materials are readily available and the apparatus can easily be installed on site.
- Photolysis of nitrated wastes has been successfully demonstrated on a pilot scale.
- In combination with other techniques (e.g., microbial degradation), efficient degradation of pollutants can be achieved.
- Treatment efficiency can be enhanced by simultaneous introduction of ozone or hydrogen peroxide.

The disadvantages of this technology are:

- The inability of UV light to penetrate and destroy pollutants in soil or in turbid or opaque solutions.
- It may be slow and ineffective under basic conditions.

Technology Status

UV photolysis has been employed for degradation of dioxins, nitrated wastes (e.g., nitrosamines), chlorinated hydrocarbons, chlorinated aromatics, pesticides, and phenolic compounds.

SECTION 6
EVALUATION OF POTENTIAL DISPOSAL TECHNOLOGIES
FOR LIQUID PROPELLANTS

On the basis of the literature review, three technologies have been identified for potential use in the disposal or degradation of HAN-based liquid propellants. The three technologies are thermal destruction, biological treatment, and photolytic degradation. Various thermal destruction processes have been developed and applied to destroy waste chemicals. These thermal processes include rotary kiln incineration, liquid injection incineration, and fluidized bed incineration. Available biological treatment processes of systems which may be applicable for the degradation of liquid propellants include composting, aerobic bioreactor, rotating biological contactor, fluidized bed reactor, and trickling filter treatment. Photolytic degradation has been accomplished using closed-loop photolytic reactors as well as solar-irradiated ponds and lagoons.

Based on the results of the review of the literature, it is apparent that each of the above technologies may potentially be useful in disposing of off-specification liquid propellant or wastes containing liquid propellant residues. However, the selection of technologies for bench- and pilot-scale evaluation must be guided by appropriate criteria to ensure that the disposal technology which ultimately is recommended does in fact meet the needs of the U.S. Army while at the same time complying with the pertinent domestic and foreign environmental regulations.

Six criteria were formulated for use in guiding the process of selecting the degradation technology that is most appropriate for bench-scale evaluation. These criteria are technical feasibility, cost effectiveness, potential for full-scale implementation, applicability in remote areas, potential for adverse environmental impact, and potential for compliance with environmental regulations. Data are not available for each of the technologies which would permit the assessment of the disposal technologies to be based upon rigorous calculations. Rather, each of the three technologies were assigned a score of 0 to 3, depending upon how well (based on best engineering judgment) the technology complied with each criterion. In the case of the potential for negative environmental impact, negative scores were assigned. As shown in Table 3, biological degradation appears to be the most appropriate technology for further study.

TABLE 6-1. RESULTS OF APPLYING EVALUATION CRITERIA TO
SELECT DISPOSAL TECHNIQUES FOR FURTHER STUDY

Criteria	Thermal	Biological	Photolytic
Technical feasibility	3	3	3
Cost-effectiveness	2	3	1
Potential for full-scale implementation	3	2	2
Applicability in remote areas	3	3	3
Potential for adverse environmental impact (negative score)	-3	-1	-1
Compliance with environmental regulations	1	3	2
	—	—	—
Total	9	13	10

SECTION 7

ENVIRONMENTAL REGULATIONS

DOMESTIC REGULATIONS

HAN-based liquid propellants exhibit the properties of a characteristically reactive hazardous waste as defined in 40 CFR 261.23(a)(6) under the Resource Conservation and Recovery Act (RCRA). This regulation states that:

A solid waste exhibits the characteristic of reactivity if... It is capable of detonation or explosive reaction if it is subjected to a strong initiating source or if heated under confinement.

Under normal usage, the propellant is not regulated under RCRA, even though it may exhibit the above properties. Several scenarios may arise, however, when the propellant is no longer usable for its original purpose and must be disposed of. It is at this point that the propellant would become a waste that is regulated under RCRA. The remainder of this section deals with the different disposal scenarios.

Noncontaminated Liquid Propellant

Liquid propellant that has exceeded a specified shelf life, is spilled, or is off-specification but is not contaminated with NDELA would have an EPA hazardous waste number of D003 (characteristic of reactivity). Characteristically hazardous wastes, such as the waste propellant, may be treated so that they no longer exhibit the characteristics that made them hazardous. In the case of HAN-based liquid propellants, demilitarization using either water or NaCl has been suggested (18) to render the liquid propellant

nonreactive; thus, the propellant would no longer be considered a hazardous waste. It is important to note, however, that the treatment process is regulated under RCRA and subject to 40 CFR 261 through 40 CFR 280 (91). The treatment facility would need to be fully regulated under RCRA and therefore require a RCRA Part B permit.

Under the RCRA regulations, once a non-NDELA propellant waste has been demilitarized to become non-hazardous, it could be passed to a sewer system and eventually to a wastewater treatment facility. However, it is suggested that given the public perception of the dangers of propellants, further treatment (e.g., aerobic biological reactor) be utilized for the complete degradation of the HAN and TEAN.

Contaminated Liquid Propellant

Liquid propellant waste or residue that has been identified as a D003 hazardous waste and is further contaminated with NDELA presents another demilitarization and disposal scenario. NDELA-contaminated propellant could also be demilitarized using water or NaCl to make it nonreactive, but it would still be classified as a RCRA hazardous waste under 40 CFR 261.33(f). NDELA is listed as a toxic waste under this section and has been given the EPA Hazardous Waste Number U173. This would require that the liquid propellant waste be further treated to deal with the NDELA (e.g., biodegradation and photolysis). It should again be emphasized that any treatment process for RCRA regulated wastes is regulated under RCRA and requires a RCRA Part B permit.

Treatment standards under RCRA have not been set for NDELA (U173) wastes. Therefore, any effluents or residues generated from the treatment

process would still be regarded as a RCRA-regulated hazardous waste, and would need to be landfilled at a hazardous waste facility.

Exclusion

An exclusion under RCRA would apply to the final disposition of the liquid propellants if the facility discharges to a publicly-owned treatment works (POTW) or operates its own wastewater treatment plant permitted under the Clean Water Act. If either of these situations exists and the waste propellant can be discharged to and treated by the treatment plant, then 40 CFR 261.4(a) applies. Under this regulation, the waste propellant and the wastewater treatment facility are excluded from regulations under RCRA. The treatment facility is still required to meet all operating and discharge standards set forth in its operating permit under the Clean Water Act.

It is important to note that the liquid propellant does not become a RCRA-regulated waste until it exceeds a specified shelf life, is spilled, goes off-specification, or becomes contaminated. In the case of the liquid propellant exceeding a specified shelf life, it is permissible to demilitarize the propellant (i.e., make it nonreactive) prior to exceeding the shelf life. This would not be considered treatment of a waste because it would still be a useful product at the time of demilitarization and therefore would not be regulated under RCRA.

FOREIGN REGULATIONS

United Kingdom

HAN-based liquid propellants would be classified as a controlled waste under the Control of Pollution Act of 1974 (92). The Special Waste Regulations

(1980) classify a controlled waste as exhibiting any one of the following characteristics:

- Explosive at 21°C
- Harmful to humans
- Medicinal product

The liquid propellant must be disposed of or stored at a licensed facility. The end product of any treatment of a controlled waste must be "environmentally safe." Dr. George Ray (92) stated that while incineration is the standard method of treatment in the U.K., he is very interested in innovative treatment technologies such as the contained biological reactor.

Dr. Ray also stated that the U.S. Army would be Crown Immune from any of the licensing procedures for treatment, storage, and disposal of the liquid propellant because the Army bases are leased from the U.K. government. The U.S. Army would not then be legally bound to comply with the controlled waste legislation, but would still be expected to dispose of the waste in a safe manner.

Federal Republic of Germany

The German Waste Management Act does not use the term "hazardous waste," but rather designates categories of waste that require special administration. These different categories include wastes that because of their nature, quantity, or condition make special demands on disposal operations which are unlike domestic (i.e., household) wastes.

HAN-based liquid-propellant waste would fall under the classification of a "particularly explosible or inflammable" material (Waste Avoidance and Waste Management Act of 1986). These wastes "may be treated, stored, and deposited only in plants or installations licensed for this purpose (waste

management facilities)" (Article 4 para 1). The Federal States within West Germany are each responsible for drawing up waste disposal plans in which special consideration is given to hazardous wastes. Since the legislation has not set any time limits for the completion of the plans, planning has advanced to different stages in the various states and would need to be evaluated for specific geographic regions within West Germany.

SECTION 8

RECOMMENDATIONS FOR FUTURE WORK

As indicated in Section 6, biological treatment has the greatest potential for accomplishing degradation of HAN-based liquid propellant residues in an economical, environmentally safe manner in a wide variety of environments. At least one report has been published which indicates that microbial degradation of HAN and TEAN is possible. However, no definitive studies have been accomplished that establish the species of microbes which have the capability to degrade HAN and TEAN, the products that arise from the microbial degradation, and the parameters that are critical for the successful degradation of the liquid propellant components. These latter data must be obtained in order to design and construct reliable HAN/TEAN biotreatment systems that can be deployed where needed all over the world.

Accordingly, PEI recommends that the next step in the development of a disposal system for HAN-TEAN liquid propellants which should be undertaken by the U.S. Army is the performance of bench scale studies to prove the feasibility of microbial degradation for mineralizing HAN and TEAN.

The approach that PEI recommends for accomplishing the recommended study is outlined below:

- A. Obtain samples of microbial cultures from hazardous waste treatment systems operated by PEI and biological treatment systems being evaluated and/or used by the U.S. Army at Badger, Radford and Holston installations.

- B. Characterize the number and type of microbes that comprise these cultures.
- C. Perform studies to determine the capabilities of the individual microbes and microbial consortia to metabolically degrade the HAN-based liquid propellant.
- D. Determine the parameters that govern the rate at which the microbes degrade the propellant (temperature, nutrients, electron acceptor type and concentration).
- E. Determine the products which result from microbial degradation of the liquid propellant. Monitor for the production of nitrosamines, especially N-nitrosodiethanolamine (NDELA).
- F. Select the most promising microbial culture and design, construct, and evaluate bench-scale systems (bioreactors) for treatment of soil and water contaminated with known concentrations of liquid propellant. Determine rate of degradation and perform optimization studies. Characterize degradation products.
- G. Perform chemical analysis to verify that aqueous effluents from bench-scale liquid propellant treatment systems are dischargeable to a Publicly Owned Treatment Works (POTW) as allowed under 40 CFR 261.4(a).
- H. Perform aquatic toxicological testing of bioreactor effluents to demonstrate that the components arising from the treatment of the liquid propellants are not a threat to the environment.
- I. Design and test transportable pilot-scale versions of bioreactors for treating propellant-contaminated solids and liquids.
- J. Perform field testing of pilot-scale reactors at selected sites, each having different environmental (climate) conditions.

Based upon the data collected in the testing program outlined above, full-scale bioreactors for treating propellant-contaminated solids and liquids can be designed and built, the necessary permits obtained, and the units deployed.

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